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PROVISIONAL SPECIFICATION

Applicant(s) :

PASMINCO LIMITED (Subject to Deed of Company
Arrangement)

Invention Title:

A PROCESS FOR UPGRADING AN ORE OR CONCENTRATE

The invention is described in the following statement:

A PROCESS FOR UPGRADING AN ORE OR CONCENTRATE

FIELD OF THE INVENTION

The present invention relates to a
5 hydrometallurgical process for upgrading a mineral ore or
concentrate to make a more-concentrated source of metal.
The present invention relates particularly, though not
exclusively, to upgrading zinc sulphide materials.

10 BACKGROUND OF THE INVENTION

The present invention was made to further improve
the recovery of zinc in the processing of an ore body at
Century in Northern Queensland. Most of the zinc is
recovered as a zinc concentrate containing zinc sulphide.
15 Typically the zinc sulphide is in the form of sphalerite
(ZnS).

The dominant process for the production of zinc
metal from zinc sulphide concentrates is the Roast-Leach-
Electrowinning (RLE) process. This process is conducted
20 in large efficient smelters that are capable of producing
zinc metal of high purity.

The electrowinning stage is energy-intensive and,
as a consequence, RLE plants are located in regions that
offer low cost electrical power which is typically some
25 distance from a remote mine site. The transport costs for
transferring concentrates and other materials to the RLE
plants, roasting performance considerations and the need
to minimise the quantities of residues generated at the
RLE site all encourage the use of high-grade zinc
30 concentrates, which are correspondingly low in impurities
such as iron and silica.

High-grade concentrates can be produced in most
zinc mines by compromising metal recovery, both at the
mining and concentrating stages. In some cases, despite
35 the rich nature of the deposits, the mineral structure of
the ores is such that suitable concentrate grades cannot
be economically produced.

Responses to this situation have seen the development of processes, such as the Imperial Smelting Process, which are capable of processing medium/low grade concentrates (in the form of mixed lead-zinc concentrates) to metals of moderate purity. Although a relatively high-cost route (requiring a sinter plant, furnace, a lead refinery and a zinc refinery), it has been a successful alternative and currently represents about 10 % of world smelting capacity. However, due to low metal prices, a number of these smelters have recently been closed.

Processes to directly leach metal sulphide ores or concentrates have been investigated. An oxidative acid ferric leach, for example, conveniently yields a zinc sulphate solution, from which (after solution purification) zinc can be electro-won. Acid leaching of concentrates, in pressure vessels, is practiced at two plants in Canada and ambient-pressure acid leaching has been introduced at another plant in Finland.

There are few mine-site hydrometallurgical plants, which indicates the importance of, and relative difficulty in obtaining, low-cost power for the electrowinning stage in remote locations.

An alternative approach is to use a mine-site hydrometallurgical process to produce a zinc chemical intermediate, with just the electrowinning stage to be conducted at the second location. From a zinc sulphate solution, for example, a precipitate of zinc sulphate ($ZnSO_4$) or basic zinc sulphate ($Zn(OH)_2 \cdot ZnSO_4$) can readily be produced. Transfer of sulphate to the electrolytic plant may, however, create a disposal problem.

It is an object of the present invention to provide an alternative process for separating the valuable metal and sulphur constituents of an ore or concentrate to make a more-concentrated source of valuable metal.

SUMMARY OF THE INVENTION

The present invention is based on the realisation that metal sulphur compounds can be dissolved away from their host mineral ore or concentrate by using an 5 ammoniacal solution under selected conditions and then selectively precipitated to make a more-concentrated source of metal.

In a situation in which the mineral ore or concentrate contains a valuable metal such as zinc in the 10 form of sphalerite, the present invention enables the zinc and sulphur constituents to be separated so that the zinc constituent can form a product that is attractive to electrolytic plants.

According to the present invention there is 15 provided a process for making a more-concentrated source of valuable metal from a mineral ore or concentrate that contains metal sulphur compounds and gangue material. The process includes the stages of:

a) selectively leaching the ore or concentrate using 20 an ammoniacal solution having a concentration selected to form soluble metal amine complexes;

b) separating the solid and liquid phases formed in stage a) with the liquid phase forming a solution including soluble metal amine complexes and the solid 25 phase including at least in part the gangue material;

c) removing ammonia from the liquid phase formed in step b) under conditions so as to selectively precipitate the valuable metal(s); and

d) separating the solid and liquid phases formed in 30 stage c) with the solid phase forming a more-concentrated source of valuable metal.

Depending on the operating conditions under which 35 stages a), and c) are carried out, the solids formed may preferentially comprise metal oxides, hydroxides and carbonates.

An advantage provided by the present invention is that valuable metals precipitated in stage c), such as

zinc, silver and copper can form a metal salt with an anion other than with a sulphur containing anion such as a sulphate.

Another advantage is that very few of the major 5 constituents of the gangue material (notably iron and silica) are soluble in an ammoniacal solution and, therefore, will form a major portion of the solid phase formed at stage b).

It is preferred that the ammoniacal solution used 10 in stage a) have a pH ranging from 7 to 10.5.

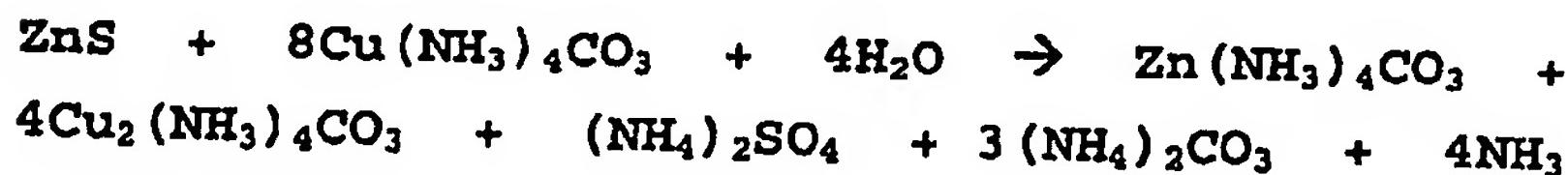
It is preferred that stage a) be carried out at a temperature ranging from 75 to 98°C when at atmospheric pressure. It is possible that stage a) may be carried out at higher temperatures and pressures.

15 It is preferred that the ammoniacal solution used in stage a) be in the form of ammonia/ammonium carbonate solution

It is preferred that a metal oxidant be used, and 20 the metal oxidant undergoes a reduction reaction to facilitate the dissolution of the metal sulphur compounds.

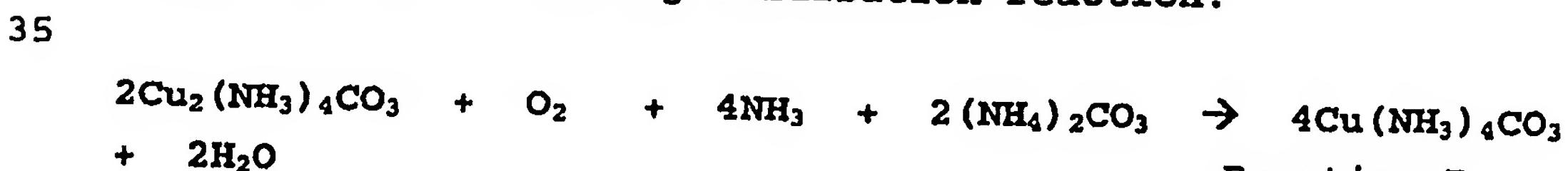
It is preferred that the metal oxidant be in the form of a cupric cation (ie Cu²⁺).

In a situation in which the valuable metal is zinc and the material being upgraded is, for example the form 25 of sphalerite (ZnS), the dissolution of sphalerite may be represented by the following reaction:



30 Reaction A

An advantage in using a divalent copper cation as the metal oxidant is that it can be regenerated using oxygen by the following oxidisation reaction:



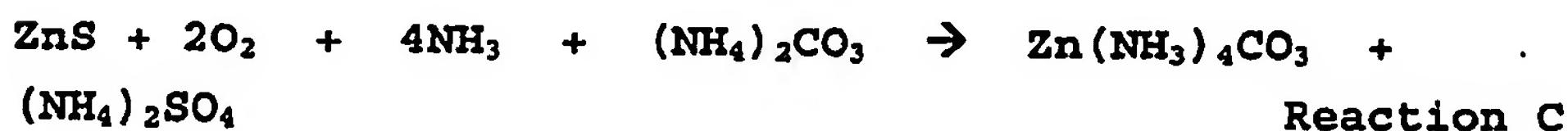
35 Reaction B

Although it is possible that Reaction B occur in a separate stage, it is preferred that an oxygen containing gas be supplied to stage a) such that Reactions A and B can occur simultaneously. Indeed, a difficulty that may 5 be encountered if oxygen is not supplied to stage a) is that the copper in solution may precipitate as a copper sulphide.

Although air may be used as the oxygen containing gas, it is preferred that a purified oxygen source be used 10 as it provides a faster reaction rate and reduces heat losses due to inert gas bubbling through the liquid.

Another reason for supplying oxygen to stage a) is that the divalent copper cations that facilitate the oxidation/reduction dissolution reactions, Reactions A and 15 B, can be regenerated in the single stage without in theory, copper being consumed. Those skilled in the art will realize that in practice an amount of make-up copper will needed to be added to stage a).

When oxygen is supplied simultaneously, the 20 overall reaction occurring at stage a) may be represented by the following reaction:



25

It is preferred that the concentration of copper cations in the ammoniacal solution used in stage a) be at least 0.25 g/L.

It is preferred that the ammoniacal solution in 30 Stage a) contains ammonia at a concentration that is sufficient to maintain the metal ions, that form amine complexes, in solution. The minimum ammonia level (for the case of zinc with copper) can be calculated by the following formulae:

35

$$[\text{NH}_3] \geq ([\text{Zn}] + [\text{Cu}] \times 8) + ([\text{SO}_4] \times 2) \quad \text{Formulae A}$$

where the concentrations are in g/L.

As an example, in a situation in which the concentration of zinc in stage a) is approximately 30 g/L, ideally the concentration of ammonia supplied in the 5 ammoniacal solution in stage a) is at least 80 g/L.

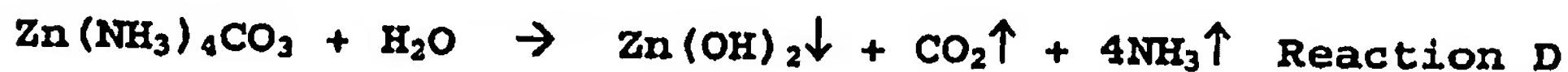
It is preferred that stage c) be carried out under conditions to minimise the precipitation of sulphur and sulphur containing compounds. To achieve this, stage c) can be carried out under conditions in which the pH is 10 equal to or greater than 7.0. As the valuable metal precipitates from the solution, the pH of the solution drops to a point at which the metal will tend to precipitate as a basic metal sulphate. This is undesirable as it effectively down-grades the suitability 15 of the precipitate for electrowinning. A pH of 7.0 is seen as a minimum pH at which the precipitation reaction can be carried out without forming detrimental amounts of metal sulphate impurities. Those skilled in the art will appreciate that other operating parameters such as 20 temperature and residence time will also influence the properties of the precipitate.

It is also preferred that stage c) be carried out at a temperature ranging from 90°C to boiling point to facilitate the removal of ammonia by 25 volatilisation/vapourization of ammonia from the liquid phase.

It is also preferred that a gas (for example, steam) be bubbled through the liquid phase of stage c) to further increase the rate at which ammonia is 30 volatilised/vapourized from the solution.

In a situation in which the valuable metal is zinc, the precipitation of a zinc metal and the vapourisation of ammonia occurring in stage c) can be represented by the following reaction:

35



Although Reaction D shows a zinc hydroxide precipitate, zinc may also be precipitated in other forms including oxides and carbonates.

In order to further increase the proportion of
5 valuable metal in the solid phase formed in stage c), it
is preferred that the process includes a stage of
calcining the solid phase recovered in stage d). The
calcination stage is a stage at which at least part of the
metal carbonates and possibly hydroxides are converted to
10 a metal oxide.

It is preferred that the calcining stage be
carried out by heating the solid phase formed in stage c)
to a temperature of 150°C or more.

It is preferred that the liquid phase from stage
15 d) be treated to precipitate sulphur and compounds
containing sulphur from the liquid phase as a salt. An
advantage provided by this preferred aspect of the
invention is that additional ammonia can be recovered for
reuse.

20 It is preferred that the liquid phase from stage
d) be treated by adding a neutralising agent to the liquid
phase. An example of a suitable neutralising agent is
lime (CaO) and the sulphur containing salt produced is
calcium sulphate (ie gypsum).

25 It is preferred that the neutralising agent
maintain the pH at about 7 during the sulphate
precipitation stage.

It is preferred that ammonia be removed from the
liquid phase in stage d) by heating the liquid phase and
30 sparging with steam.

The sulphate precipitation stage may be
represented by the following reaction:



It is preferred that the ammonia volatilised/vapourized from either stage c) and/or the stage for precipitating the sulphate ions be recovered and reused in stage a).

5 It will be appreciated by a person skilled in the art of the present invention that stages a) to d), or any of the other stages described above may be carried out consecutively or disjunctively and may, for example, be carried out at different plant sites.

10 The present invention also encompasses a solid phase made substantially of a metal oxide and any of the other solid and liquid phases including the gypsum formed in sulphate precipitation stage made according to the process of the present invention.

15 The present invention also encompasses a plant including at least two reactor vessels for carrying out stages a) and c) and at least two solid/liquid separation devices for carrying out stages b) and d) of the process.

20 DETAILED DESCRIPTION OF THE INVENTION

A detailed description of a preferred embodiment of the present invention will now be described with reference to Figure 1.

25 The description is in the context of a zinc refining plant. However, the present invention is not confined to treating this valuable metal and is equally applicable to other valuable metals, such as copper or lead.

30 In terms of process flow, the preferred embodiment includes an ammonia leaching stage 11 that is supplied with a zinc containing feed material such as an ore or concentrate, an ammoniacal solution and oxygen. The ammoniacal solution and feed material form a slurry in the 35 leaching stage 11. Once reacted in the leaching stage 11, the slurry is fed to a solid/liquid separator 12 in which the liquid phase is separated from the solid phase which

is largely constituted by insoluble gangue material. The liquid phase is then supplied to a zinc precipitation stage 13 in which a zinc containing solid phase is precipitated and thereby forms a slurry. The slurry is 5 then fed to another solid/liquid separator 14 in which the liquid phase is separated from the solid phase. The solid zinc containing phase is then fed to a calcining stage 15 before being refined in an electrowinning process (which is not shown in Figure 1). The liquid phase formed in 10 separator 14 is further treated in a sulphate precipitation stage 16 to further recover ammonia. The sulphate may be precipitated in the form of gypsum and can be supplied to agricultural fertiliser manufacturers.

Ammonia and carbon dioxide are vapourized in the 15 zinc and sulphate precipitation stages 13 and 16, and are recycled back the ammonia leaching stage 11.

The operational characteristics of each stage will now be described in more detail.

The ore concentrate fed to the ammonia leaching 20 stage 11 comprises sphalerite (ZnS) and gangue material including iron and silica.

The ammoniacal solution comprises disassociated 25 copper amine complexes. In particular both Cu^{1+} and Cu^{2+} cations can form soluble amine complexes as shown in Reaction A set out above.

According to Reaction A, the cupric cations function as an oxidising agent such that the zinc constituents of the feed material form a soluble amine complex. There are several advantages in using copper as an oxidising agent. 30 Firstly, it forms soluble amine complexes in a pH range of 7.0 to 10.5 at a temperature ranging from 80 to 95°C, whereas the gangue in the feed material is substantially insoluble at these conditions. Secondly, the copper oxidising agent can be conveniently regenerated using 35 oxygen according to Reaction B set out above.

The overall oxidation/reduction reaction that dissolves sphalerite in leaching stage 11 is represented by Reaction C set out above.

In some instances sphalerite may be directly 5 oxidised by oxygen according to the following reaction:



However, it will be appreciated that the 10 "products" formed by Reactions C and F will exist in solution as disassociated ions and ammonia carbonate will exist in solution as a mixture of bicarbonate, carbonate and free ammonia.

In the instance when the raw material includes 15 zinc carbonate, it can be dissolved according to the following reaction:



20 Ammonia is distributed in solution between the copper and zinc amine complexes, ammonium bicarbonate, ammonium sulphate and as hydrolysed ammonia. The total ammonia level in solution must be sufficient to maintain the zinc and copper ions in solution. The minimum ammonia 25 level required can be estimated by the following formulae in which the concentrations of zinc, copper and sulphate are the concentrations present in stage 11.

$$[\text{NH}_3]_{\min} = ([\text{Zn}] + [\text{Cu}]) \times 8 + ([\text{SO}_4] \times 2)$$

30 When the concentration of zinc present in stage a) is 30g/L, the minimum recommended concentration of NH₃ in the ammoniacal solution is 80 g/L.

The zinc leaching rate in stage 11 is temperature 35 dependent. A temperature of between 80 and 95°C has been adequate for trials conducted to date. It may be beneficial to conduct the leaching stage 11 at higher

temperatures and pressures to achieve a higher reaction rate.

The leaching stage 11 is also dependent on sufficient oxygen being available to regenerate Cu²⁺ ions.

- 5 In principle air could be used, but purified oxygen is preferred as it gives faster reaction rates and the heat losses will be lower.

- If the dissolved oxygen level is not maintained during the course of the leach reaction, copper is likely 10 to be precipitated, removing it from an active role according to the following reaction:



- 15 Any gases formed, or introduced with the oxygen, will need to be vented from the leach reactor. As ammonia is quite volatile, there will be ammonia losses with these gases, requiring offgas treatment using condensers or water scrubbers (not illustrated in Figure 1).

- 20 Once the zinc has been dissolved, and un-reacted material removed in the solid/liquid separator 12, the objective is to recover the zinc.

The zinc amine complex can be broken by heating the solution to (near) boiling and sparging with steam.

- 25 This drives off ammonia and carbon dioxide and precipitates zinc as the hydroxide/hydrated oxide according to Reaction D set out above. Zinc carbonates may also be present in the solid phase.

- As can be seen from the Figure 1, the ammonia and 30 carbon dioxide are recyclable back to the leaching stage 11 to at least in part form the ammoniacal leach solution. Makeup ammoniacal solution may also be fed to the leach stage 11 when needed.

- As the ammonia is removed, the zinc will 35 precipitate, ideally as an oxide/hydroxide according to Reaction D. The zinc may also precipitate as a basic zinc carbonate according to the following reaction:

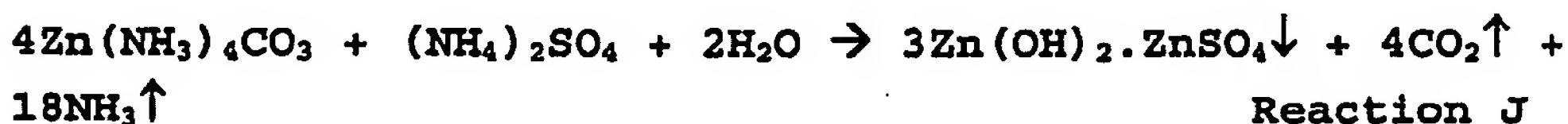


Reaction I

5 While reaction I does not contaminate the zinc product with sulphate ions, reaction I reduces the overall grade of the precipitate because the zinc content of the solids in the hydroxide form is about 66 % whereas the basic zinc carbonate only contains about 60% zinc.

10 In addition, Reaction I causes a slight drop in pH as the zinc precipitates, which becomes more marked as the precipitation nears completion. As the pH drops there is a greater tendency for zinc to precipitate as a basic sulphate according to the following reaction:

15



Reaction J

20 The selected end point for the precipitation reaction in stage 13 is a trade-off between maximising the zinc precipitation and minimizing sulphate contamination of the precipitate.

25 The slurry formed in the zinc precipitation stage 13 is then fed to a solid/liquid separator 14 and the solid phase containing the zinc constituents is fed to the calcining stage 15.

30 The calcining stage 15 effectively converts zinc carbonates and possibly hydroxide to zinc oxide. This will reduce the mass to be transported to the electrowinning refinery and will reduce losses of ammonia. The calcining stage 15 is carried out by heating the precipitate to about 150 °C.

35 The liquid phase supplied to the sulphate precipitation stage 16 contains significant quantities of ammonium sulphate and can be precipitated to form a by-product that can be used by agricultural fertiliser manufacturers. This is achieved by boiling and/or steam

sparging the liquid. A neutralising agent, such as lime or limestone, is added to maintain the correct pH. The choice of which neutralising agent to use is an economic one, both are effective. Gypsum is formed in stage 16 as 5 the by-product of the acid-base reaction, represented by Reaction E set out above.

The slurry in stage 16 can be fed directly to a tailings dam.

Set out below is description of a trial carried 10 out according to the preferred embodiment of the present invention.

Stage 1: Ammonia leach

An ammoniacal leaching stage was conducted at 85 15 °C for 5 hours, with oxygen sparging. The starting material was a low-grade concentrate containing 15 % Zn, in the form of sphalerite. The pulp density was 200 g dry solids/litre solution. Copper was added at a level of 0.5 g/l Cu as a solution of copper tetra-amine bicarbonate. 20 The pH was maintained between 8.5 and 9.0 by addition of a mixture of ammonium hydroxide and ammonium hydrogen carbonate, giving a free ammonia level of 70 g/l. The final solution contained 20 g/l Zn, 30 g/l NH₃, and 35 g/l SO₄. The zinc extraction was 93 %.

25

Stage 2: Zinc precipitation

The solution from the previous example was heated to 100 °C and sparged with oxygen (experimentally, a convenient carrier gas) for 2 hours. Over this time, a 30 precipitate formed and the pH dropped to 6.8.

The precipitate was analysed and shown to contain 90 % Basic Zinc Carbonate, 2.3 % Basic Copper Carbonate, 6 % Basic Zinc Sulphate and 0.8 % other inerts (silica, gypsum).

35 The residual solution contained 1 g/l zinc and 0.3 g/l copper. This represents 97 % recovery of zinc in this stage.

Stage 3: Sulphate precipitation

The solution from Example 2 was again heated to 100 °C and sparged with oxygen for 2 hours. Limestone was 5 added to maintain the pH at approximately 7.0. Over this time, a precipitate formed and assays show this to be a mixture of calcium carbonate and calcium sulphate. The final liquor contained less than 0.01 g/l each of zinc, copper and ammonia.

10

Stage 4: Calcination

The dry solids collected from the test described in stage 2 were heated in a furnace at 190 °C overnight. A 10 % decrease in mass was observed, corresponding to a 15 conversion to zinc oxide ($ZnO \cdot H_2O$).

It will be appreciated by those skilled in the art of the present invention that modifications may be made to the preferred embodiment of the invention without departing from the spirit and scope of the invention.

